PTO/SB/17 (06-07) Approved for use through 06/30/2007. OMB 0651-0032

Fee (\$)

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\$1,370

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Effective on 12/08/2004. Complete if Known es pursuant to the Consolidated Appropriations Act, 2005 (H.R. 4818). 10/714,230 **Application Number** TRANSMIT Filing Date November 14, 2003 For FY 2007 First Named Inventor SUN, Sam-Shajing **Examiner Name** Hall, Asha J. Applicant claims small entity status. See 37 CFR 1.27 Art Unit 1709 **TOTAL AMOUNT OF PAYMENT** 1,370.00 036021.0001 Attorney Docket No. METHOD OF PAYMENT (check all that apply) Check Credit Card Money Order None Other (please identify): ✓ Deposit Account Deposit Account Number: <u>50-0766</u> Deposit Account Name: For the above-identified deposit account, the Director is hereby authorized to: (check all that apply) Charge fee(s) indicated below Charge fee(s) indicated below, except for the filing fee Charge any additional fee(s) or underpayments of fee(s) Credit any overpayments under 37 CFR 1.16 and 1.17 WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038. **FEE CALCULATION** 1. BASIC FILING, SEARCH, AND EXAMINATION FEES **EXAMINATION FEES FILING FEES SEARCH FEES Small Entity Small Entity Small Entity Application Type** Fee (\$) Fee (\$) Fee (\$) Fees Paid (\$) Fee (\$) Fee (\$) Fee (\$) Utility 300 150 500 200 250 100 Design 200 100 100 130 50 65 Plant 200 100 300 150 160 80 300 Reissue 150 500 600 250 300 Provisional 200 100 0 0 O 0 2. EXCESS CLAIM FEES Small Entity

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Each claim over 20 (including Reissues)

3. APPLICATION SIZE FEE

Fee Description

If the specification and drawings exceed 100 sheets of paper (excluding electronically filed sequence or computer listings under 37 CFR 1.52(e)), the application size fee due is \$250 (\$125 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).

Total Sheets Number of each additional 50 or fraction thereof Fee Paid (\$) /50 = (round up to a whole number) x 4. OTHER FEE(S) Fees Paid (\$) Non-English Specification, \$130 fee (no small entity discount)

SUBMITTED BY			
Signature		Registration No. (Attorney/Agent) 43,659	Telephone 757-499-8800
Name (Print/Type)	M. Bruce Harper		Date June 19, 2007

Other (e.g., late filing surcharge): Petition for Exceptance of Unintentionally Delayed Claim for Priority

This collection of information is required by 37 CFR 1.136. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 30 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

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Firm Name	Williams Mullen							
Signature								
Printed name	M. Bruce Harper							
Date	Date June 19, 2007 Reg. No. 43,659							
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This collection of information is required by 37 CFR 1.5. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and1.14. This collection is estimated to 2 hours to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.



# 6-20-07

DAC

### IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: Sam-Shajing SUN Confirmation No.: 2469 Application No. 10/714,230 1709 Art Unit: Filed: November 14, 2003 Examiner: Asha J. Hall For: PHOTOVOLTAIC DEVICES Attorney Docket No: 036021.0001 **BASED ON A NOVEL** BLOCK COPOLYMER

Mail Stop Petition Commissioner for Patents P.O. Box 1450 Alexandria, VA 22313-1450

# PETITION FOR THE ACCEPTANCE OF UNINTENTIONALLY DELAYED CLAIM FOR PRIORITY UNDER 37 CFR § 1.78(a)

#### Dear Sir/Madam:

Applicant hereby petitions for the acceptance of the unintentionally delayed claim for priority under 37 CFR 1.78(a) for the above-referenced pending application. The above referenced pending application was filed with a priority claim referencing a provisional patent application, but this reference included a typographic error in the serial number of such reference (i.e., the incorrect reference to U.S. Provisional Patent Application Ser. No. 60/428,108, wherein the underscored 8 should have been a 6). This typographic error of a single digit was identified upon examination. At no time did Applicant intentionally delay correction of such priority claim; the entire delay was unintentional. In summary, Applicant intended to claim priority to U.S. Provisional Patent Application Ser. No. 60/426,108. With the Commissioner's acceptance, the Applicant intends to amend the above referenced application with such a correction.

This petition is accompanied by a priority claim reference to the prior-filed provisional application, U.S. Provisional Patent Application Ser. No. 60/426,108, in

Attachment A. A copy of the U.S. Provisional Patent Application Ser. No. 60/426,108 is provided in Attachment B.

The Commissioner is therefore respectfully requested to accept this correction of the priority claim of the referenced pending application. A fee of § 1,370 is believed to be due for this petition. Please charge the required fee to Williams Mullen Deposit Account No. 50-0766.

Date: June 19, 2007

Customer Number: 45309

(757) 499-8800

Respectfully submitted, WILLIAMS MULLEN

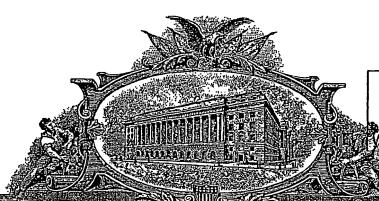
M. Bruce Harper

(Reg. No. 43,659)

### Attachment A

The present application claims priority from U.S. Provisional Patent Application Ser. No. 60/426,108, filed November 14, 2002, which is hereby incorporated by reference.

### Attachment B



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TO AUL TO WHOM THESE: PRESENTS SHAVE COME:

UNITED STATES DEPARTMENT OF COMMERCE United States Patent and Trademark Office

January 12, 2004

THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE.

APPLICATION NUMBER: 60/426,108 FILING DATE: November 14, 2002

RELATED PCT APPLICATION NUMBER: PCT/US03/36538

By A COM

By Authority of the COMMISSIONER OF PATENTS AND TRADEMARKS

Y Kgwynnce T. LAWRENCE Certifying Officer

PRIORITY DOCUMENT

SUBMITTED OR TRANSMITTED IN COMPLIANCE WITH RULE 17.1(a) OR (b)

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# PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53 (c).

		INVE	NTOR(S)	<del></del>					
Given Name (first and m	iddle[if any])	Family Name		1014	Residence				
Sam-Shajing	·	Sun	• .	427 Willo	(City and either State or Foreign Country) 427 Willow Brook Way Chesapeake VA 23320				
Additional Inventor	rs are being i	named on the	separate	<del></del>					
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Firm or Individual Name	M. Bruce Harper								
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Address		bus Center, Suite	e 900			34.75			
City	Virginia Bea		State	VA T	/A ZIP 23462				
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SUBSTITUTE FOR PTO/S8/17 (2-89)
Approved for use through 09/30/2000. OMB 0851-0032
Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

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FEE TRANSMITTAL	Application Number					
Patent fees are subject to annual revision on October 1.	Filing Date					
These are the fees effective October 1, 1997.	First Named Inventor Sun, Sam-Shajing					
Small Entity payments <u>must</u> be supported by a small entity statement, otherwise targe entity fees must be paid. See forms PTO/SB/09-12.	Examiner Name					
See 37 C.F.R. §§ 1.27 and 1.28.	Group / Art Unit					
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M. BRUCE HARPER

Typed or printed name of person mailing correspondence

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Title: A Photovoltaic Device Based on Conjugated Block Copolymers

Inventor: Sam-Shajing Sun

A Photovoltaic Device Based on Conjugated Block Copolymers

BACKGROUND OF THE INVENTION

Field of the Invention:

The present invention relates to the field of photovoltaic or opto-electronic devices. More particularly, this invention relates to cost effective, lightweight, and flexible shaped "plastic" photo detectors and "plastic" solar cells (renewable and clean energy generation), etc.

**Background** 

Photovoltaic (PV) is a process where light is absorbed by a media and is then converted into a voltage or electric current. When light strikes certain materials, the photons in the light excite electrons in the material. In some materials, there are free electrons that are released by the interaction with the photon; the movement of that electron leaves a hole. The flow of the electron, along with the resulting holes creates electric current. Most of the PV cells used today are based on inorganic semiconductor materials such as silicon, although other materials, such as Gallium Arsenide, Cadmium Telluride, Copper Indium Diselenide are also used.

The typical silicon based solar cell uses a semiconductor pn-junction. The cell comprises semiconductor layers, one of which is n-doped (doped with atoms of excess valence electrons) and the other is p-doped (doped with atoms lacking a valence electron); their interface forms a pn-junction. The n-doped layer is characterized by Specification 1 of 9

Title: A Photovoltaic Device Based on Conjugated Block Copolymers

Inventor: Sam-Shajing Sun

excess electrons, while the p-doped layer is characterized by holes. In other words, the n-doped layer is a donor (D) of electrons, and the p-doped layer is an acceptor (A). Initially the doped materials reach equilibrium across the pn-junction. When sunlight strikes the material, the light is absorbed in the excitation of the excess electrons, which are released and create a charge separation along the pn-junction; a transport of electrons and holes creates the electrical current that is collected by electrodes.

The high cost of manufacturing traditional inorganic photovoltaic materials and devices has led to significant research into alternative photovoltaic materials, as well as how to configure those materials within the solar cells. Additionally, improved efficiency could lower the lifetime cost and make photovoltaic devices a more commercially attractive and environmentally friendly energy alternative. One area of research is the use of organic materials to fabricate solar cells, such as using semi-conducting conjugated polymers, liquid crystalline structures, etc. Organic materials, including polymers, are relatively inexpensive, lightweight, flexible, and easily manufactured in comparison to their inorganic counterparts.

However, semi-conducting polymers work differently from inorganic semiconductors. Semi-conducting polymers are long molecules that have repeating structures and with alternating single and double carbon-carbon bonds, and are referred to as being "conjugated." The double bonds (also called  $\pi$  bonds) within conjugated polymers generate a highest occupied molecular orbital (HOMO) that is typically filled with  $\pi$  electrons, and a lowest unoccupied molecular orbital (LUMO) that is typically

Title: A Photovoltaic Device Based on Conjugated Block Copolymers

Inventor: Sam-Shajing Sun

empty without light or other forms of excitation. The HOMO or LUMO of each double bond in a conjugated polymer backbone interact with each other and form HOMO and LUMO bands, the energy difference between the two bands is generally called band gap, or sometimes also called the "optical gap".

Most conjugated polymers appear to have a band gap that lies in the range of 1—3 eV, which makes them ideally suited for light harvesting or photovoltaic devices working in the visible light range. The photo-induced electron transfer and charge (electron-hole) separation observed in conjugated organic composites of the donors (electron-donating or p-type organic species) and acceptors (electron-withdrawing or n-type organic species) provide an alternative to traditional inorganic solar cells.

The mechanism for an organic approach to high efficiency light harvesting or photovoltaic conversion has been developed. Specifically, in organic photovoltaic materials, for instance, light generated excitons (e.g., electron-hole pairs) can typically diffuse 20 nm in their lifetime. The charges (electrons and holes) can be separated at the contact interface between the donors and acceptors, where for donor excitons, the electrons are transferred from donor's LUMO to the acceptor's LUMO and for acceptor excitons, the holes transferred from acceptor's HOMO to the donor's HOMO, provided that the corresponding energy level differences between the donor and acceptor are big enough to overcome the exciton binding energy (typically 0.5 eV). Next, and mainly due to the asymmetry of the photovoltaic cell, the electrons travel and are collected at the negative electrode, and holes travel and are collected at the positive electrodes. One of

Title: A Photovoltaic Device Based on Conjugated Block Copolymers

Inventor: Sam-Shajing Sun

the main scientific challenges for a high efficiency organic photovoltaic device is to fabricate a nano structure where both the donor and acceptor phases have dimensions within the typical organic exciton diffusion range (about 20 nm), yet are continuous between the two electrodes.

#### **DESCRIPTION OF THE INVENTION**

The present invention is a potentially efficient organic photovoltaic device made of a –DBA- or an analogous block copolymer system, where D is a donor derivatized conjugated polymers, oligomers, or equivalent (also referred as "conjugated donor block"), A is an acceptor derivatized conjugated polymer, oligomer, or equivalent (also referred as "conjugated acceptor block"), B is a non-conjugated (such as aliphatic) bridge unit. The said block polymer system may also be embodied in, refer to, or be represented as –ABD-, –DBAB-, -ABDB-, -BDBA-, -BABD-, -DBABD-, -ABDBA-, etc.

The present invention comprises the structure and fabrication process of a polymer or "plastic" thin film photovoltaic device that possesses benefits of lightweight, flexible shape, cost effectiveness, and potentially very high power conversion efficiency in comparison to current commercial inorganic semi-conductor based photovoltaic devices. This "plastic" photovoltaic device has the following features:

1) A conjugated donor block (D) is covalently connected with a conjugated acceptor block (A) via a short non-conjugated bridge unit (B) to form a --DBA- or its analog type block copolymer chemical structure, as shown in Figure 1. Preliminary experimental

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work has shown the -DBAB- type to be a useful embodiment. Those skilled in the art

will readily see that a variety of configurations could be produced for specific

applications or specifications. Preferably, the donor and acceptor blocks should be

chosen, configured, or built in such a way that the band gap of both donor and acceptor

phases in solid states substantially match the optical radiation energy of the intended

applications or devices. This -DBA- and its analog type polymer backbone structure or

"Primary Structure" can be realized via common organic design and synthesis.

2) Additionally, both the donor and acceptor conjugated block backbones may be self-

assembled in a solid thin film state to form a  $\pi$ -orbital stacked or adjacent block chain

closely packed structures, as shown in Figure 2, as in many conjugated polymer

systems, so that the  $\pi$ -orbitals between adjacent backbones are well coupled or

overlapped to each other. This may be called a "Secondary Structure".

3) Additionally, the donor and acceptor block should be sufficiently different from each

other, so that in solid thin film state, donor and acceptor blocks will be able to phase

separate from each other as seen in many block copolymer systems. The donor and

acceptor separated phases may be self-assembled to form a columnar or "Honeycomb"

shaped structures, as is the general case known in many di- or tri-block copolymer

systems.

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It is known that the incompatibility between the blocks leads to the formation of many unique micro- or nano-phase separated and ordered structures, including, but not limited to, lamella, columnar, cubic centered lattice, etc., and a specific phase separated structure is determined by chemical composition, size of each block, temperature, and other factors. For instance, a recent report of MEH-PPV/Polystyrene-C<sub>60</sub> donor/acceptor di-block copolymer system indeed exhibited a "honeycomb" shaped nano structure.

Each donor phase column should interface with at least one acceptor column, and vice versa. The diameter of each column should be approximately within the corresponding effective exciton diffusion length of the respective donor or acceptor blocks (typically about 20 nm).

Finally, a thin layer of donor block may be coated on one side of the columnar or "Honeycomb" structure in perpendicular to the column direction in order to form a positive side of the photovoltaic device, and a thin layer of acceptor block will likewise coated on the other side of the "Honeycomb" to form a negative side of the PV device. Other forms of aligning or directing charge as is known in the art will serve as well. Finally, a conducting electrode with a work function close to, or substantially appropriate to the HOMO levels of the donor placed in contact to the donor (positive) layer side of the device will collect holes, and a conducting electrode with a work function close to, or substantially appropriate for the LUMO levels of the acceptor placed in contact to the acceptor layer (negative) side to collect electrons. At least one electrode should be

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transparent to the intended light radiation. This may be called "Tertiary Structure" of the said PV cell, as shown in Figure 3.

In the present invention, a –DBAB- type block copolymer system has already been synthesized and characterized recently, where D is an alkyloxy donor derivatized poly-(1,4)-phenylenevinylene (PPV), abbreviated as "RO-PPV", A is a sulfone acceptor derivatized PPV, abbreviated as "SF-PPV-I", and B is a non-conjugated aliphatic bridge unit. Preliminary electron microscopic study has revealed interesting regular nanophase separated morphological pattern in a drop dried –DBAB- film. A donor or acceptor derivatized polythlophenes, or other similar type materials, may also be used as the conjugated blocks. A non-conjugated bridge unit provides an energy barrier between the bands of the donor and acceptor blocks in order to prevent a convenient electron-hole recombination. The bridge also makes the donor or acceptor rigid blocks less vulnerable to distortion, and more convenient to self-assemble. Conjugated  $\pi$  orbital distortion due to molecular thermal vibrations or backbone twist typically interrupts conjugation and therefore reduces charge mobility.

In summary, the backbone structure –DBA- and its analogs may be called a "Primary Structure". Since the  $\pi$  orbital overlap between rigid blocks are useful for charge mobility, this self-assembly morphology between blocks could be called a "Secondary Structure". Finally, the block copolymer "honeycomb" morphology provides

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smooth "tunnels" for charge transportation to the respective electrodes. The "honeycomb" structure may be sandwiched between a thin layer of donor film (in contact with a positive electrode), and a thin layer of acceptor film (in contact with a negative electrode) so that an efficient asymmetric polymeric photovoltaic device is thus formed. The sandwiched "honeycomb" structure can be called a "Tertiary Structure". Another advantage of this system is that the interfacial area and the phase size can be tuned via block copolymer segment size, therefore, the opto-electronic conversion

#### **CLAIMS**

efficiency can be easily optimized via materials design and synthesis.

What is claimed is:

- 1. A photovoltaic primary structure comprising:
  - a conjugated donor block,
  - a conjugated acceptor block, and
  - a non-conjugated bridge covalently coupling said donor block and said acceptor block.
- 2. The photovoltaic primary structure as described in claim 1, wherein a second non-conjugated bridge is covalently coupled to one of either said acceptor block or said donor block, and said second non-conjugated bridge is capable of coupling to other such photovoltaic primary structures to form a repeating chain.

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3. A photovoltaic secondary structure comprising a plurality of primary structures in a  $\pi$  orbital stack and closely packed morphology.

- 4. A photovoltaic tertiary structure comprising a plurality of secondary structures in a phase separated collumnar nano-structure.
- 5. A photovoltaic tertiary structure as described in claim 4, further comprising a donor thin layer at a first end of such collumnar nano-structure and an acceptor thin layer at an opposing second end of such collumnar nano-structure, wherein said donor thin layer and said acceptor thin layer are oriented to such collumnar nano-structure so as to form an asymmetric geometry.
- 6. A process for producing a photovoltaic primary structure comprising the steps of producing a conjugated donor block,

  producing a conjugated acceptor block, and covalently coupling said donor block to said acceptor block with a non-conjugated bridge.

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